UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND INVESTIGATION OF ELECTRICAL AND THERMAL PROPERTIES OF CONDUCTING POLYMER POLYPYROLE AND POLYPYROLE/MULTIWALL CARBON NANOTUBE COMPOSITES

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FS 2012 14

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By

AFARIN BAHRAMI SHABESTARI

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

June 2012

Dedicated to my husband, parents, sisters and my daughter Andia.

Without their understanding and support, I would never have completed this project.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

SYNTHESIS AND INVESTIGATION OF ELECTRICAL AND THERMAL PROPERTIES OF CONDUCTING POLYMER POLYPYROLE AND POLYPYROLE/MULTIWALL CARBON NANOTUBE COMPOSITES

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Chairman: Professor Zainal Abidin Talib, PhD

Faculty: Science

Conducting polymer materials based on Polypyrrole (PPy) and Polypyrrole/ Multiwall carbon nanotube (PPy/MWNT) nanocomposite were synthesis by using chemical reaction process. PPy/MWNT composites were prepared with different concentrations of MWNT ranging from 0% to 20%.

X-ray diffraction (XRD) revealed that no crystalline peak appeared for PPy, because of its amorphous feature. The X-ray data of the composites showed spectra similar to those observed from the pure PPy matrix, indicating that PPy has completely covered the MWNT. The Fourier transform infrared spectroscopy (FTIR) spectra of PPy and PPy/MWNT composites demonstrated nearly identical numbers and positions of IR absorption bands because of the matrix layer of polypyrrole has absorbed most of the IR spectra. Results from field emission scanning electron microscopy (FESEM) and transmission electron microscopy

(TEM) showed that the diameter of MWNTs has increased and confirmed the presence of carbon nanotubes inside the composite.

The transport properties has been studied by measuring Hall mobility (μ_H) and Hall coefficient (R_H) of polypyrrole and PPy/MWNT nanotubes samples with different MWNT concentration using van der Pauw technique. The μ_H decreased as below for samples with 0%, 4%, 8%, 12%, 16% and 20% MWNT content from 100 to 300K respectively: 40.987 to 16.231cm^2/V.s, 20.291 to 14.329cm^2/V.s, 17.992 to 2.891cm^2/V.s, and 8.228 to 0.926cm^2/V.s, 6.329 to 0.541cm^2/V.s and 3.688 to 0.081cm^2/V.s. The R_H reduced for samples with 0%, 4%, 8%, 12%, 16% and 20% MWNT content from 100 to 300K respectively as below: 2163.944 to 68.989cm^3/C, 12.797 to 0.303cm^3/C, 8.099 to 0.254cm^3/C, 1.432 to 0.042cm^3/C, 0.956 to 0.023cm^3/C and 0.463 to 0.003cm^3/C. The magnetic field dependency of R_H revealed that it was inversely proportional with the applied magnetic field. The R_H reduced with applied magnetic field (1 to 10KG) from 86.59 to 6.863cm^3/C, 21.105 to 2.707cm^3/C, 7.5592 to 1.337cm^3/C, 0.025 to 0.002cm^3/C and 0.019 to 0.002cm^3/C for the samples with 0%, 4%, 8%, 12%, 16% and 20% MWNT content respectively. The μ_H decrement with magnetic field (1 to 10KG) was as below: 188.118 to 15.162cm^2/V.s, 62.673 to 8.048cm^2/V.s, 79.112 to 14.114, 53.471 to 3.380, 0.535 to 0.051, and 0.492 to 0.054 for the samples with 0%, 4%, 8%, 12%, 16% and 20% MWNT content respectively.

The electron paramagnetic resonance (EPR) results showed that the Peak-to-peak linewidth (ΔH_{pp}) value decreased in the order PPy-MWNT-20wt% (37.606mT) > PPy-MWNT-16wt% (49.328mT) > PPy/MWNT-12wt% (95.970) > PPy/MWNT-8wt% (120.879mT) > PPy/MWNT-4wt % (139.926mT) > pure PPy (150.831mT)

at room temperature. The measurement revealed that the spin concentration (Ns) of the PPy/MWNT with the various MWNT content was larger than that of the pure PPy (2.07×10^6, 3.42×10^6, 12.7×10^6, 30.7×10^6, 33.8×10^6 and 41.96×10^6 spin g^{-1} for 0%, 4%, 8%, 16% and 20% MWNT content). Thermal stability (decomposition temperature was 116.04, 120.69, 126.03, 128.86, 141.18 and 170.96^oC for samples with 0wt%, 4wt%, 8wt%, 12wt%, 16wt% and 20wt% MWNT content) and also thermal diffusivity (0.103, 0.118, 0.141, 0.186, 0.224 and 0.265mm^2/S for samples with 0wt%, 4wt%, 8wt%, 12wt%, 16wt% and 20wt% MWNT content respectively) of the composite increased with the decrease of the feeding mass ratio of pyrrole to MWNTs.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTISIS DAN KAJIAN ELEKTRIK DAN TERMA KOMPOSIT POLIMER KONDUKSI POLYPYRROLE/CARBON TIUB NANO DINDING BERGANDA

Oleh

AFARIN BAHRAMI SHABESTARI

June 2012

Pengerusi: Professor Zainal Abidin Talib, PhD

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Bahan polimer konduksi berasaskan Polypyrrole (PPy) dan komposit nano Polypyrrole/tiub nano karbon dinding berganda (PPy/MWNT) telah disintesis dengan menggunakan proses tindak balas kimia. Komposit PPy/MWNT yang disediakan dengan kepekatan yang berbeza MWNT antara 0 hingga 20%.

Untuk PPy, tiada kemunculan puncak hablur PPy dikesan kerana ciri amorfusnya. Data sinar-X bagi komposit menunjukkan spektra sama seperti yang diperhatikan dari matriks PPy tulen, yang menunjukkan bahawa MWNT telah diselaputi oleh PPy. Spektrum spektroscopi jelmaan Fourier inframerah (FTIR) PPy dan komposit PPy/MWNT menunjukkan jumlah dan kedudukan jalur penyerapan IR hampir sama kerana lapisan matriks PPy telah menyerap kebanyakan spektrum IR. Keputusan dari mikroskopi medan pancaran imbasan elektron (FESEM) dan

mikroskopi tranmisi elektron (TEM) menunjukkan bahawa diameter MWNTs telah meningkat dan mengesahkan kehadiran tiub nano karbon di dalam komposit.

Sifat pengangkutan telah dikaji dengan mengukur mobiliti Hall (μ_H) dan pekali Hall (R_H) sampel polypyrrole dan PPy / MWNT tiub nano dengan kepekatan MWNT berbeza menggunakan teknik van der Pauw. μ_H menurun seperti di bawah untuk sampel dengan 0%, 4%, 8%, 12%, 16% dan 20% kandungan MWNT dari 100 hingga 300K: 40.987 kepada 16.231cm^2/Vs, 20.291 kepada 14.329cm^2/Vs, 17.992 untuk 2.891cm^2/Vs, dan 8.228 kepada 0.926cm^2/Vs, 6.329 kepada 0.541cm^2/Vs dan 3.688 untuk 0.081cm^2/Vs. R_H menurun untuk sampel dengan 0%, 4%, 8%, 12%, 16% dan 20% kandungan MWNT dari 100 hingga 300K masing-masing seperti di bawah: 2163.944 kepada 68.989cm^3/C, 12.797 untuk 0.303cm^3/C, 8.099 kepada 0.254cm^3/C, 1.432 untuk 0.042cm^3/C, 0.956 kepada 0.023cm^3/C dan 0.463 untuk 0.003cm^3/C. Pergantungan medan magnet R_H mendedahkan bahawa ia adalah berkadar songsang dengan medan magnet digunakan. Pekali Hall menurun dengan medan magnet yang digunakan (1 hingga 10KG) dari 86.59 6.863cm^3/C, 21,105 untuk 2.707cm^3/C, 7.5592 1.337cm^3/C, 0.025 0.002cm^3/C dan 0.019 kepada 0.002cm^3/C untuk sampel masing-masing dengan 0%, 4%, 8%, 12%, 16% dan 20% kandungan MWNT. Penyusutan μ_H dengan medan magnet (1 ke 10KG) adalah seperti berikut: 188.118 kepada 15.162cm^2/Vs, 62.673 kepada 8.048cm^2/Vs, 79.112 kepada 14.114, 53.471 kepada 3.380, 0.535 kepada 0.051, 0.492 kepada 0.054 untuk sampel masing-masing dengan 0 %, 4%, 8%, 12%, 16% dan 20% kandungan MWNT.

Keputusan EPR menunjukkan bahawa nilai lebargaris puncak ke puncak (ΔH) menurun dalam turutan PPy-MWNT-20wt% (37.606mT) > PPy-MWNT-16wt%

(49.328mT) > PPy/MWNT-12wt% (95.970) > PPy/MWNT-8wt% (120.879mT)> PPy/MWNT-4wt% (139.926mT) > tulen PPy (150.831mT) pada suhu bilik. Pengukuran menunjukkan bahawa kepekatan spin (Ns) PPy / MWNT dengan pelbagai kandungan MWNT adalah lebih besar daripada PPy yang tulen (2.07×10^6, 3.42×10^6, 12.7×10^6, 30.7×10^6, 33.8×10^6 dan 41.96×10^6 spin g^{-1} untuk 0%, 4%, 8%, 12%, 16% dan 20% kandungan MWNT). Kestabilan terma (suhu pereputan adalah 116.04, 120.69, 126.03, 128.86, 141.18 dan 170.96^oC untuk sampel dengan 0wt%, 4wt%, 8wt,% 12wt%, 16wt% dan 20wt% kandungan MWNT) dan juga keresapan terma (0.103, 0.118 , 0.141, 0.186, 0.224 dan 0.265mm^2/S untuk sampel dengan 0wt%, 4wt%, 8wt%, 12wt%, 16wt% dan 20wt% kandungan MWNT) komposit meningkat dengan penurunan nisbah pyrrole dengan MWNT.

ACKNOWLEDGEMENTS

Thanks to Allah for my good health, strength and patience during the undertaking of this project.

I would like to express my sincerest appreciation to my research supervisor, Associate Professor Zainal Abidin Talib, PhD for giving me the opportunity to work in his lab and for his advice and encouragement throughout this entire project.

I wish to give special thanks to my committee members Professor Wan Mahmood Mat Yunus, PhD and Professor Anuar Kassim, PhD for their suggestions, during the past few years.

I am grateful to all the staff of Faculty of Science for helping me feel home here at UPM. Special thanks go to Mrs Rusnani Amirudin, Mr Mohd Zain Mohd Yusof, Mr Mohd Roslim, Mrs Zaidina Md. Daud, Ms Nor Azlina Shari, Mr Shaharuddin, Mrs Kamsiah Alias and other science officers whose names are not mentioned in this section for their assistance in analyzing the samples and their valuable effort and time.

It is a pleasure to acknowledge my colleagues Mahnaz, Josephine, Khor, Amir, Reza, Aina, Ira, Sabri, Abdullah, Emma, Firdaus, Nordin, Jamileh, Ina and Chang who have been helpful and willing to share their knowledge, skills and experience.

Last but not least, without the love, support, guidance, and encouragement of my husband, my family, my daughter and specially my dear sister Marjan, this moment would never have been realized. I would like to express my deepest gratitude to all my family members. I love you and thank you so much.

I certify that an Examination Committee has met on … … 2012 to conduct the final examination of Afarin Bahrami Shabestari on her Doctor of Philosophy thesis entitled "Synthesis and Investigation of Electrical and Thermal Properties of Conducting Polymer Polypyrrole and Polypyrrole/Multi wall Carbon nanotube Composites" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanain Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or other institutions.

AFARIN BAHRAMI SHABESTARI

Date: 18/June/2012

TABLE OF CONTENTS

		Page
ABSTRACT		iii
ABSTRAK		vi
ACKNOWLEDGEMENTS		ix
APPROVAL		xi
DECLARATION		xiii
LIST OF TABLES		xvii
LIST OF FIGURES		xviii
LIST OF ABBREVIATIONS		xxv
CHAPTER		
1	**INTRODUCTION**	1
1.1	Conducting Polymers	1
1.2	Carbon Nanotubes	4
1.3	Composite of Conducting Polymer and Carbon Nanotube	5
1.4	Research Problem	7
1.5	Objectives of the Research	7
1.6	Outline of the Thesis	8
2	**LITERATURE REVIEW**	9
2.1	Conducting Polymers	9
2.2	Polymerization Methods	12
2.3	Conducting Polymer/ Carbon Nanotube Composites	15
2.4	Electrical Conductivity	19
2.5	Conduction Mechanism	26
2.6	Hall Effect	29
2.7	Electron Spin Resonance	31
2.8	Thermal Stability	32
2.9	Morphology of PANI–CNT Composites	33
2.10	FTIR	34
2.11	XRD	36
2.12	Thermal Conductivity of Conducting Polymer Composites	37
3	**METHODOLOGY**	39
3.1	Introduction	39
3.2	Sample Preparation	39

3.2.1 Materials 39
3.2.2 Preparation of Polypyrrole and Polypyrrole/MWNT Conducting Polymer Pellets 40
3.3 Sample Characterization 41
3.3.1 X-ray Diffraction (XRD) Measurement 42
3.3.2 Thermal Diffusivity Measurement 42
3.3.3 Thermogravimetric Analysis (TGA) 44
3.3.4 Fourier Transform Infrared Spectroscopy (FTIR) 44
3.3.5 UV-VIS-NIR Spectroscopy 45
3.3.6 Hall Effect Measurements 47
3.3.7 Field Emission Scanning Electron Microscope (FESEM) Analysis 50
3.3.8 Transmission Electron Microscopy (TEM) 50
3.3.9 Electron Spin Resonance (ESR) 51
3.3.10 High Temperature DC Conductivity Measurement 53
3.3.11 Four-Point Probe Technique 53
3.3.12 Conductivity Calculation 55

4 RESULTS AND DISCUSSION 59
4.1 Introduction 59
4.2 XRD Measurement 60
4.3 Molecular Structure of PPy-MWNT Composite 61
4.4 UV-VIS-NIR Spectroscopy of PPY and PPy/MWNT composites 64
4.4.1 Using UV-Vis-NIR Spectra for Calculation the Optical Band Gap of PPy and PPy/MWNTs Composite 67
4.5 Morphological Study of PPy and PPy/MWNT Composites 71
4.5.1 Field Emission Scanning Electron Microscopy (FESEM) 71
4.5.2 Transmission Electron Microscopy (TEM) 73
4.6 Electrical Conductivity of PPy-MWNT Conducting Polymer Nanocomposite 76
4.7 Temperature Dependence of Electrical Conductivity of PPy-MWNT Conducting Polymer Composite 77
4.7.1 Low Temperature Dependence 78
4.7.2 High Temperature Conductivity 86
4.8 Study of the Hall Coefficient of PPy and PPy-MWNT at Low Temperature 87
4.9 The study of the Hall Mobility of PPy and PPy-MWNT at Low Temperature 91

4.10 The Investigation of the Hall Coefficient of PPy and PPy-MWNT at Different Magnetic Field 96
4.11 The Study of the Conductivity of PPy and PPy-MWNT at Various Magnetic Fields 100
4.12 The Study of the Mobility of PPy and PPy-MWNT at Various Magnetic Fields 103
4.13 Magnetoresistance 106
4.14 Electron Spin Resonance (ESR) 109
4.14.1 Peak-to-Peak Linewidth (ΔH_{pp}) 110
4.14.2 Spin Concentration (Ns) 111
4.14.3 g-factor 113
4.15 Thermogravimetric Analysis (TGA) 113
4.16 Thermal Diffusivity 116

5 CONCLUSION 121
5.1 Introduction 121
5.2 Future Studies 124

REFERENCES **126**
APPENDIX **141**
BIODATA OF STUDENT **147**